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IMPROVING SPECTRAL FITS OF ABSORPTION DATA TAKEN WITH AN ARRAY DETECTOR: WAVELENGTH "LINEARIZATION"

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SEPTEMBER 1990

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13. ABSTRACT (Maximum 200 words)

Wavelength "linearization" is incorporated into a least squares fitting routine tailored for optical absorption spectra taken with a photodiode array. In general, the wavelength linearization algorithm improves the quality of the fits; in some cases, the standard deviation of the fits is improved by more than a factor of two.

14. SUBJECT TERMS

Absorption, Solid Propellant, Combustion, Temperature, Flame, OH Concentration, Photodiode Array, Monochromator, Wavelength Linearization

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TABLE OF CONTENTS

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LIST OF FIGURES

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I. INTRODUCTION

We have been conducting optical diagnostic measurements on solid propellant combustion for the past few years. While analyzing some recent OH absorption spectra[2,3] with a least squares fitting program, an inconsistency appeared, *i.e.*, the computer fits of OH absorption data taken under high spectral resolution resulted in a larger statistical uncertainty than the fits for spectral data taken with half the spectral resolution. The source of this inconsistency has been identified and corrected using a wavelength "linearization"[1] method for an array detector.

II. EXPERIMENTAL

Premixed CH_4/N_2O laminar flames and nitramine propellant flames have been probed by detecting rotationally resolved absorptions of the OH molecule around 306.4 nm. Details of the experimental apparatus appear elsewhere[2-5] and only the optical detection segment will be described here. The optical path for light produced by a 1 kw mercury-xenon arc lamp is shown on Fig. 1. This broadband light is focussed and

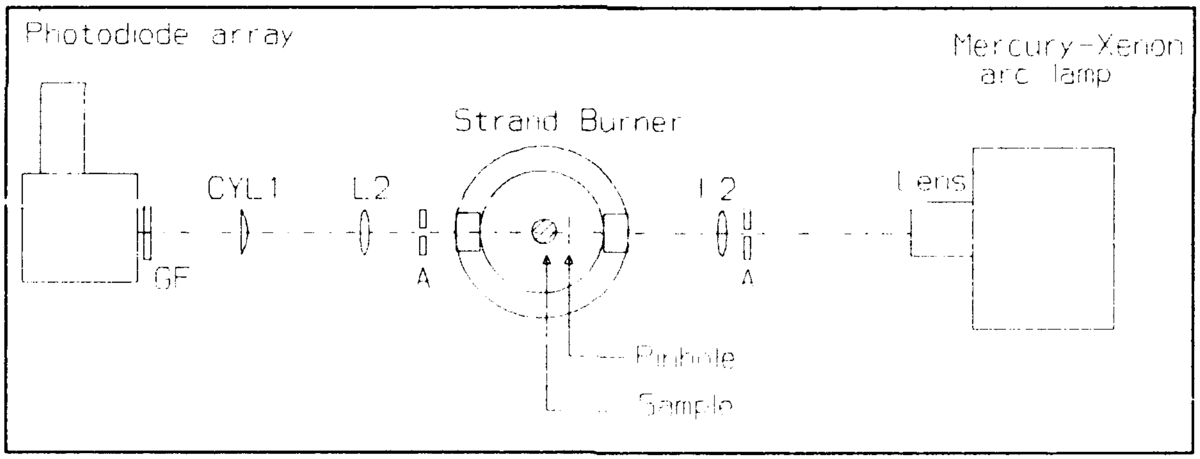

Figure 1 The light path for the optical absorption experiments. The glass filter (GF) was used to eliminate first order light when operating the spectrometer second order; the sample is either a premixed flame or propellant.

apertured with lenses and adjustable irises. A 150 micron pinhole provides the final spatial restriction before reaching the sample region. Light transiting the sample region is line focussed onto a monochromator with a cylindrical lens. This Czerny-Turner type monochromator (model HR-320 manufactured by J-Y Optical Systems) has a 0.32 m focal length and a 2400 grooves/mm holographic grating. The monochromator was operated in second order to adequately resolve the rotational absorption lines occurring in the $A^2\Sigma^+$-$X^2\Pi_i$ (0,0) vibrational band system of OH. First order light is rejected by a glass filter

(Schott UG-11) placed in front of the monochromator. A 0.025 mm entrance slit gives a spectral resolution (FWHM) of 0.03 nm for second order operation and a 0.06 nm resolution for first order operation.

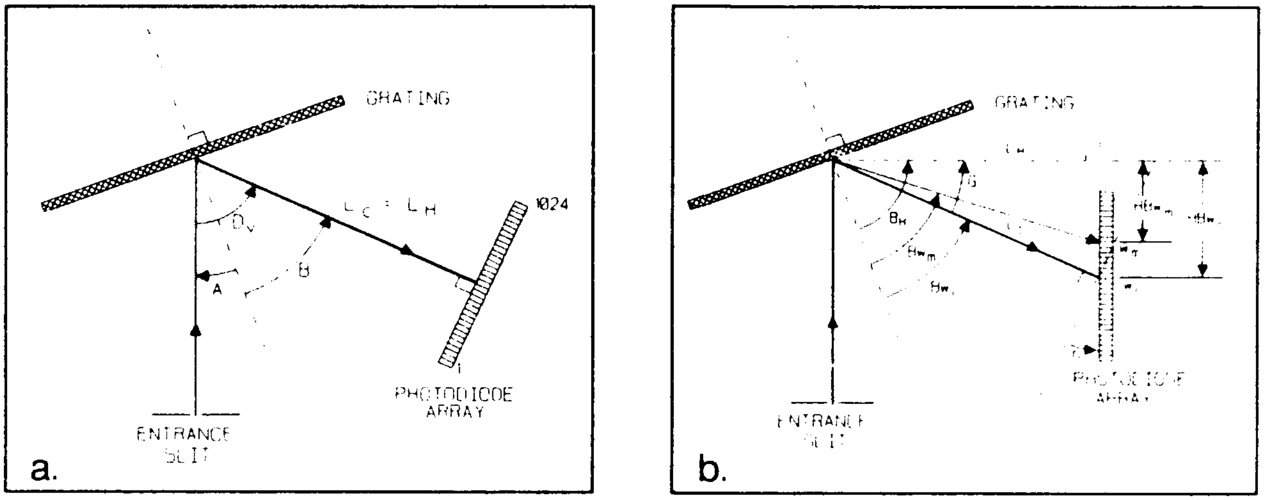

Figure 2 Configuration where monochromator focal plane is (a.) normal to the central wavelength of and (b.) inclined at an angle G with respect to the central wavelength of the photodiode array.

The light detector is a photodiode array with 1024 photodiodes of 0.025 mm width. About 700 of these photodiodes receive amplified light from a microchannel plate intensifier. The geometry of the detector with respect to the diffraction grating of the monochromator (see Fig. 2) determines the non-linearity produced in the conversion of photodiode position to wavelength. The tilt angle (G) determines the extent of this non-linearity. In the data analysis section which follows, an algorithm is given for linearizing the wavelength.

III. DATA ANALYSIS

When a monochromator is used with an array detector, the relationship between wavelength and pixel (photodiode) position may not be linear. The following abbreviated data analysis describes such a case for a Czerny-Turner type configuration and is taken from an optical spectroscopy tutorial by Lerner and Thevenson.[6]

The grating equation can be written as

$$\sin A + \sin B = 10^{-6} knw \tag{1}$$

and

$$D_v = B - A \tag{2}$$

All of the symbols are shown in Figs. 2a and 2b and described in Table 1. The angle of

Table 1. Symbols, definitions, units and values when appropriate.

Symbol	Definition	Units	Values for HR-320
A	Angle of incidence	degrees	
B	Angle of diffraction	degrees	
D_v	Deviation angle	degrees	24
G	Tilt angle	degrees	2.4
k	Diffraction order	integer	
n	Grating groove density	grooves/mm	2400
w	Wavelength	nanometers	
w_c	Wavelength at center of array	nanometers	
w_m	Wavelength at position m	nanometers	
Bw_m	Angle of diffraction at wavelength m	degrees	
L_f	Focal length of monochromator	mm	320
L_H	Perpendicular distance from grating to the focal plane	mm	319.719
B_H	Angle from L_H to the normal to the grating	degrees	
HBw_m	Distance from the intercept of the normal to the focal plane to the wavelength w_m	mm	
HBw_c	Distance from the intercept of the normal to the focal plane to the wavelength w_c	mm	13.4
Pwd	Nominal width of the pixel	mm	0.0245
Pm	Pixel number at wavelength w_m	integer	
Pc	Pixel number at wavelength w_c	integer	

incidence can be expressed as

$$A = \sin^{-1}[10^{-6} knw/2\cos(D_v/2)] - D_v/2. \qquad (3)$$

For a specific wavelength, w_m, Eqn. (1) can be rewritten as

$$w_m = [\sin A + \sin Bw_m]10^{6}/kn \qquad (4)$$

where

$$Bw_m = B_H - \tan^{-1}(HBw_m/L_H) \tag{5}$$

and

$$HBw_m = HBw_c - Pwd(Pm - Pc). \tag{6}$$

Eqn. (4) is now used to compute the wavelength for the least squares fitted OH spectra presented in the results section; previous published results[2-5] used a fixed wavelength increment per pixel. The pixel width has been allowed to vary in the fitting procedure; although the nominal width between pixels is given as 0.025 mm the best fits occurred for values of about 0.0245 mm.

The main purpose of this diagnostic technique is to extract temperature and concentration from absorption spectra by using a non-linear least squares fitting procedure with an equation of the form

$$I_{tr} = \int S(w,w_o)I(w)dw \tag{7}$$

where I_{tr}, the integrated light transmitted, is a function of w_o, the index frequency of the diode; $S(w,w_o)$ is an instrument function appropriate for the spectral resolution of the detection system; and $I(w)$ is the transmitted intensity of a group of lines for a given species. A much more complete explanation of the absorption technique and the fitting procedure is described elsewhere.[2,3,7,8]

IV. RESULTS

Figures 3 and 4 show spectral absorption data taken in an atmospheric pressure CH_4/N_2O laminar flame. These absorptions are from rotationally resolved transitions in the A-X (0,0) vibrational band system of OH. The data are represented by dots and the non-linear least squares fit to the data is a solid line. Conditions under which these absorption spectra were taken plus the fitted values obtained for the temperature and concentration are given in Table 2. The main difference† between the spectral data of Fig. 3 and Fig. 4 is that the monochromator was operating in second order for Fig. 3, therefore, these data are much better resolved. Contrary to intuition, however, the standard deviation of the overall fit and of both the temperature and concentration is higher for the better resolved

†It is also seen that the values of the temperature and concentration are different. This result is not surprising since there was no quantitative control on flame conditions and the data for Figs. 3 and 4 were obtained on different days.

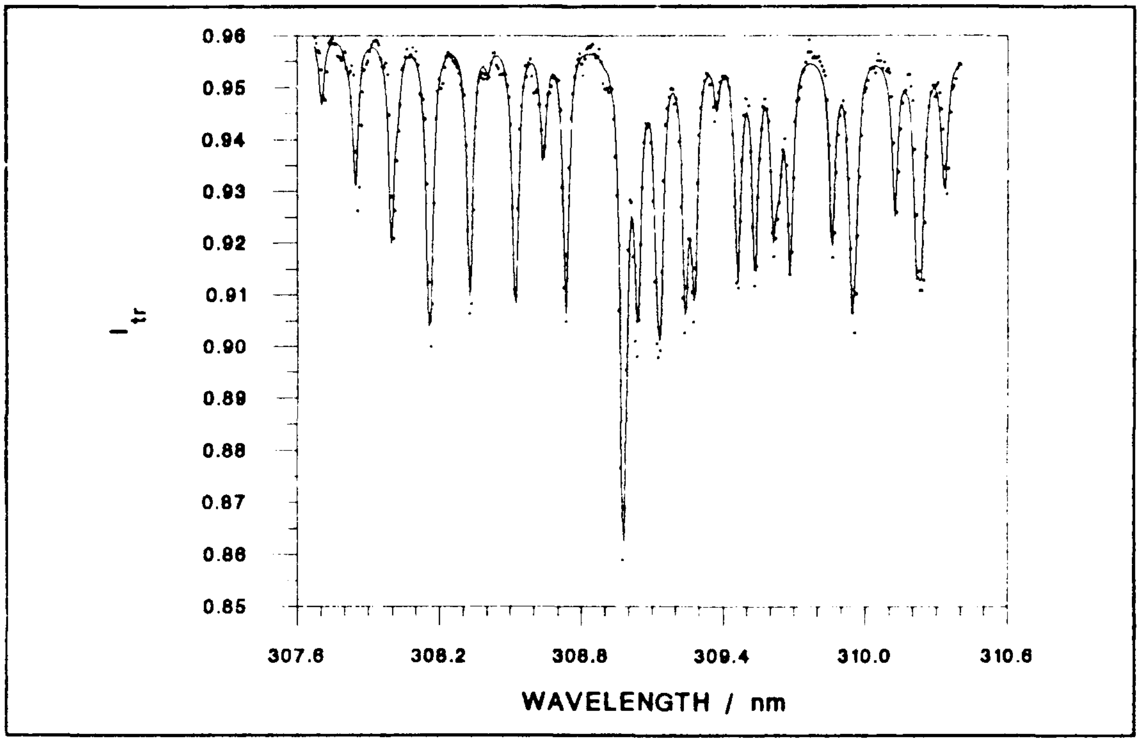

Figure 3 Rotationally resolved, second order (uncorrected) OH absorption spectrum taken 1 mm above the burner surface of the premixed flame; solid line, least squares fit for values in Table 2.

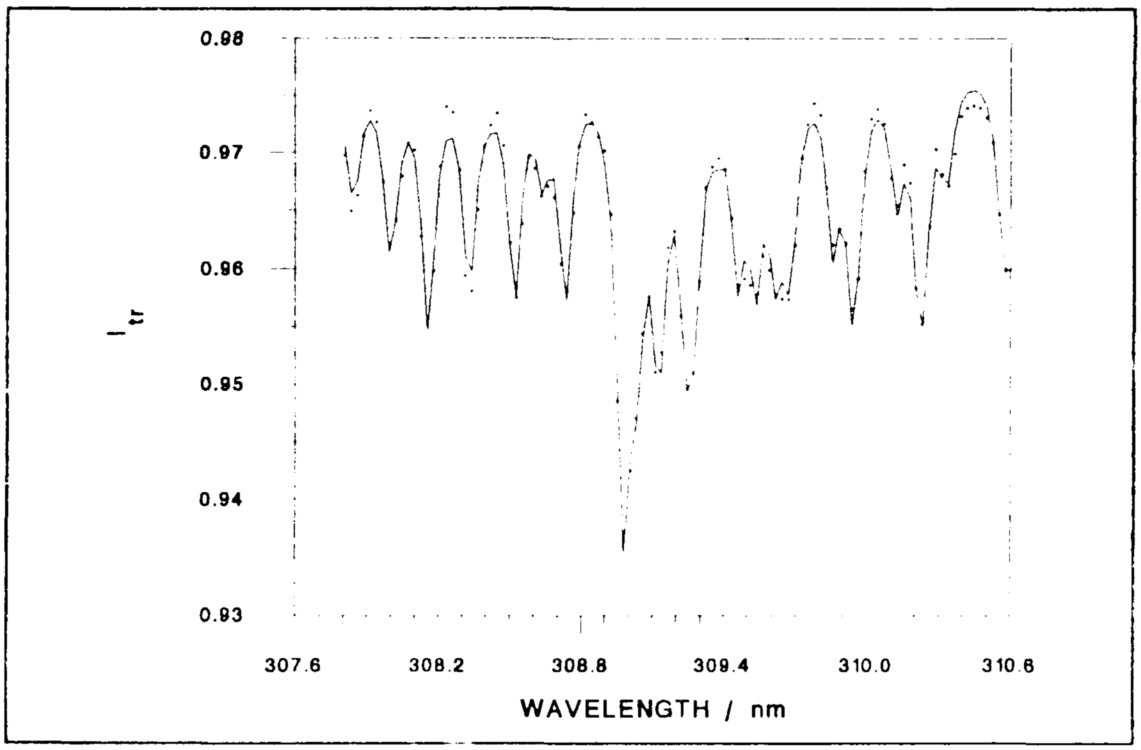

Figure 4 Same conditions as Fig. 3 except here the monochromator was operated in first order.

data (see graph captions). This observation prompted our use of the wavelength correction algorithm discussed in the data analysis section. The data of Fig. 3 were subsequently refitted incorporating this algorithm and are plotted along with the wavelength corrected fit on Fig. 5. Although the standard deviation of the fit has dropped by more than a factor of two, it is difficult to see the differences in the quality of the fits when comparing Figs. 3

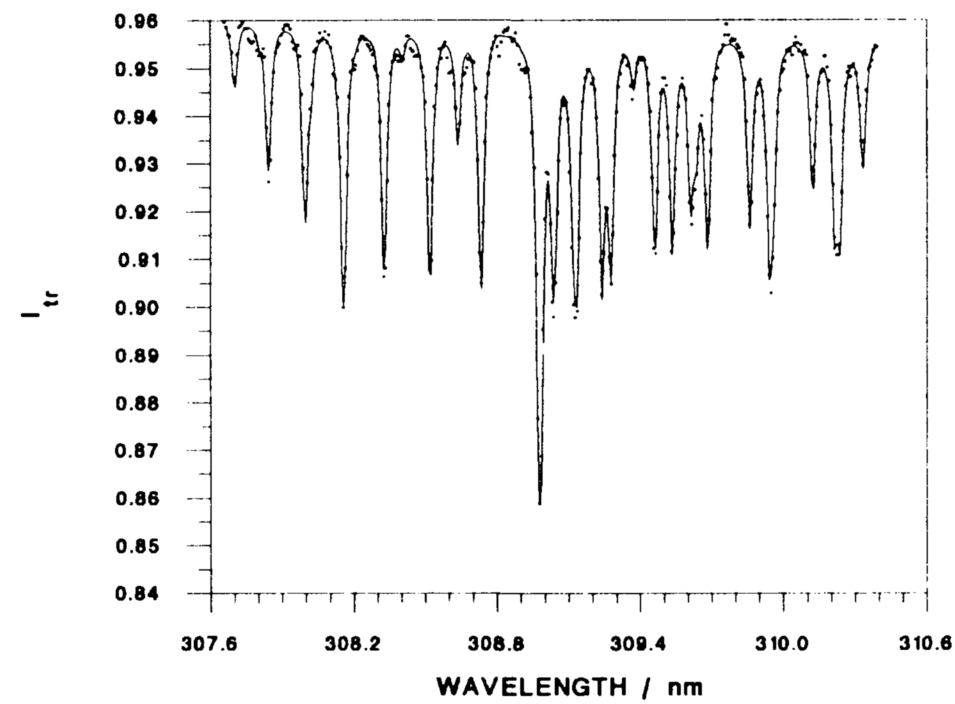

Figure 5 Same conditions as Fig. 3 except the data were fitted using wavelength linearization.

and 5. However, plots of the absolute difference (data point value - calculated value) for both Figs. 3 and 5 clearly show the improvement attained when incorporating this wavelength linearization algorithm, and these are given on Figs. 6 and 7, respectively. The absolute value differences shown in Fig. 6 (uncorrected) are about twice as large as in Fig. 7 (corrected). Moreover, the data of Fig. 7 appear random whereas the data of Fig. 6 are structured indicating the presence of a systematic error.

The data of Fig. 4 were obtained in first order for the same wavelength range covered on Fig. 3. This means that for the data of Fig. 4 the spatial extent of the dispersed light is about half that for the conditions of Fig. 3, hence, the nonlinearity should be less influential. This is confirmed by comparing the standard deviation of the least squares fit of the low resolution spectrum with and without the wavelength linearization. For spectra obtained with the grating operating in first order, no appreciable improvement was realized by incorporating wavelength linearization. Thus, for the low resolution first order flame

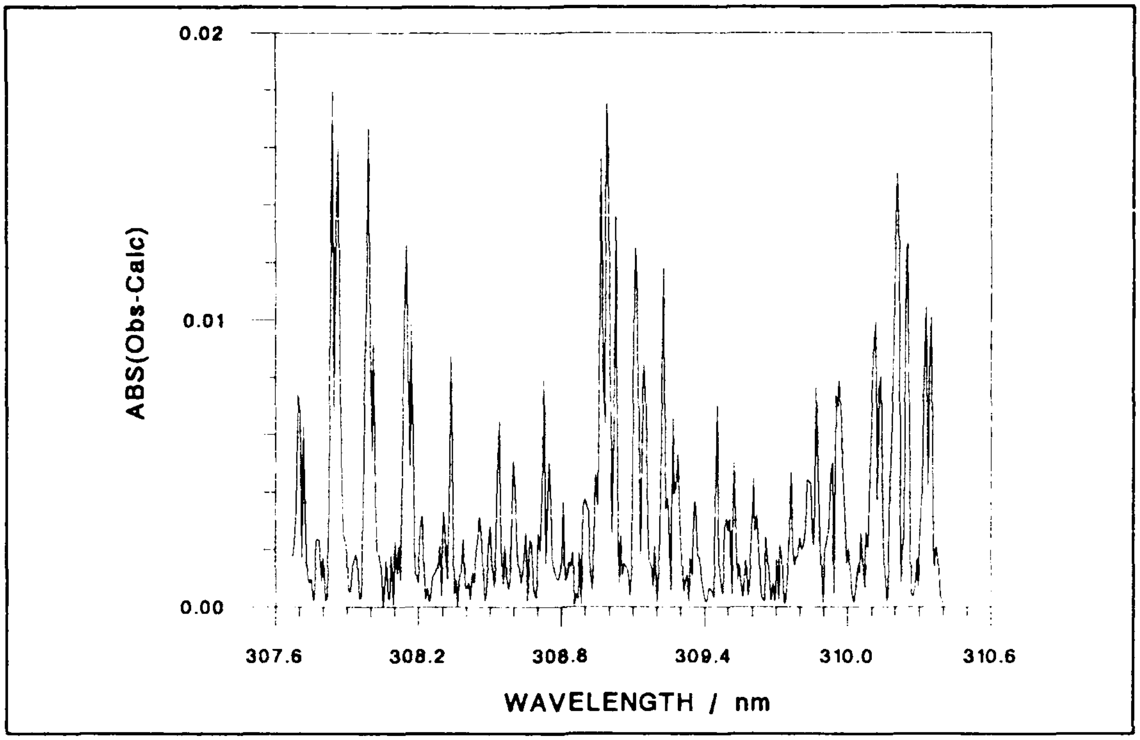

Figure 6 Plot of the absolute difference of the observed values and the fitted values versus wavelength for the conditions of Fig. 3.

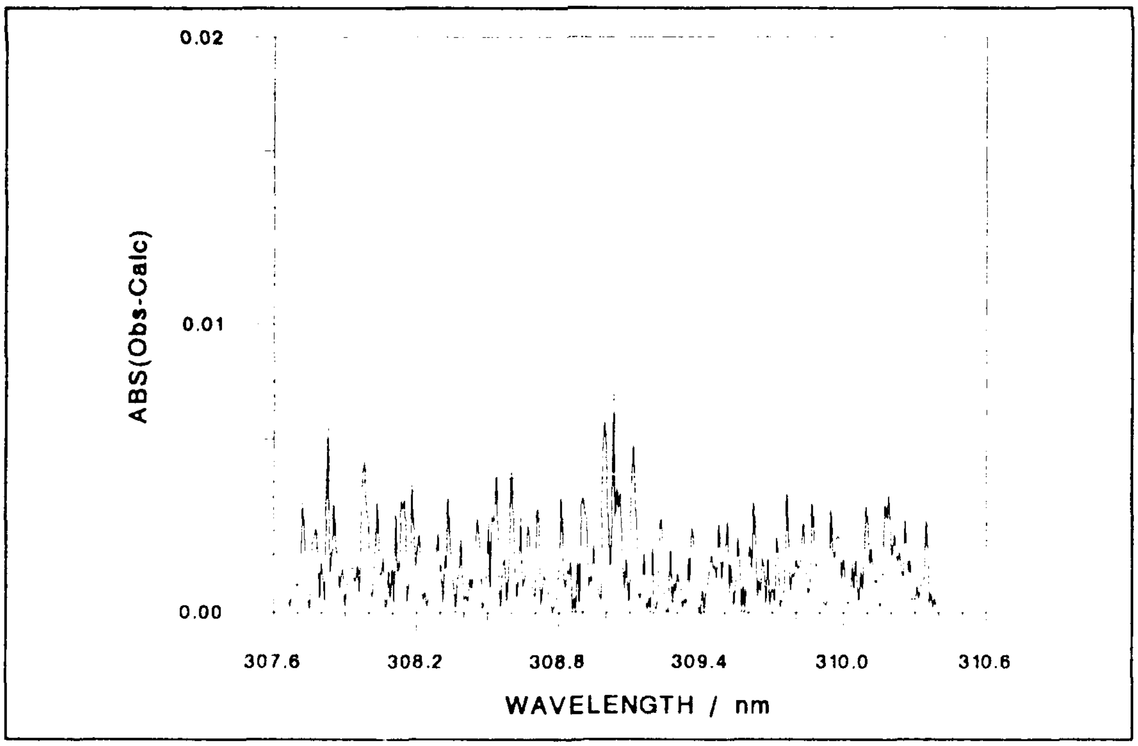

Figure 7 Plot of the absolute difference of the observed and the fitted values versus wavelength for the conditions of Fig. 5.

data of Fig. 4, nonlinearity in the wavelength does not notably influence the quality of the fit.

Wavelength linearization has also been applied to the same kind of OH absorption data taken in propellant flames burning in 1.5 MPa nitrogen. This is a significantly more hostile environment than a premixed laminar flame, and there is a limited amount of time for accumulating the data. One of the best propellant spectra that we have been able to obtain is shown on Fig. 8. Although the second order propellant data is noisier than the flame data, the linearization is shown to still lower the uncertainty in the fitted values (see Table 2).

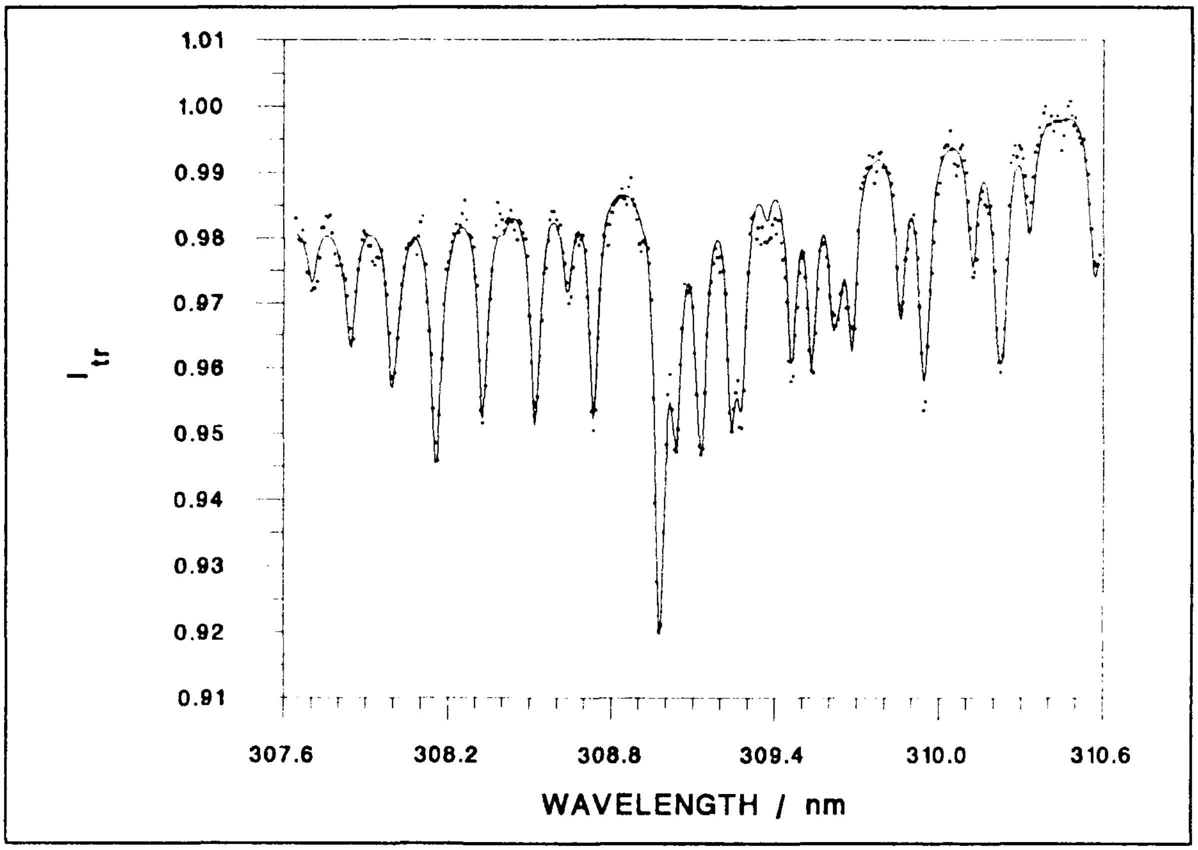

Figure 8 Rotationally resolved OH spectrum: 0.4 to 0.9 mm above the propellant surface, burning in 1.5 MPa nitrogen: data acquisition time, 1.6 sec.; monochromator, second order; data fitted using linearization.

Table 2. Conditions for which OH absorption spectra were least squares fitted to obtain temperatures and concentrations together with their standard deviation.

Sample	Order	Wavelength Linearization	OH Concentration (molecules/cc)	Temperature (K)	Comments
Flame	2	no	$3.67 \pm 0.14 \times 10^{16}$	2214 ± 85	data and fit on Fig. 3
Flame	1	no	$3.05 \pm 0.08 \times 10^{16}$	2378 ± 64	data and fit on Fig. 4
Flame	2	yes	$3.66 \pm 0.07 \times 10^{16}$	2212 ± 37	shown on Fig. 5 same data as Fig. 3
Flame	1	yes	$3.07 \pm 0.07 \times 10^{16}$	2380 ± 64	fit not shown same data as Fig. 4
Propellant	2	no	$2.29 \pm 0.07 \times 10^{16}$	2346 ± 75	not shown
Propellant	2	yes	$2.33 \pm 0.06 \times 10^{16}$	2420 ± 54	data and fit on Fig. 8

V. CONCLUSION

The wavelength linearization process described in the text has significantly improved the fitting of data taken by a photodiode array. In the case of OH absorption spectra taken in a steady-state premixed flame, the standard deviation of the fit was lowered by more than a factor of two. As the spectral resolution decreases or other sources of noise become larger, the relative importance of the linearization effect decreases.

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